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CATALYTIC AGENT DEGRADATION ON OXIDE FILMS AND IN MICROHETEROGENEOUS SOLUTION SYSTEMS

Second Interim Report

by

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Research pursued under contract no. DAJA 45-90-C-0007 entitled "Catalytic Agent Degradation on Oxide Films and in Microheterogeneous Solution Systems" emphasized the **destructive oxidation** of simulant compounds in oxidant containing aqueous solutions

Both **photocatalytic and dark decompositions** of the **organophosphate** compounds diethylbenzylphosphonate (DBP) and diethylethylphosphonate (DEP) were investigated in the presence of hydrogen peroxide as oxidant. The role of colloidal TiO_2 and **ferric sulfate** as **promoters** for the **complete mineralisation** of the agent was explored.

Fundamental studies under the same experimental conditions on the **degradation** of the aromatic species **nitro-o-xylene (NOX)** were likewise undertaken in order to more clearly elucidate the aromatic ring breaking mechanism.

The combined effects of dark catalysis and band gap excitation were investigated.

ORGANOPHOSPHATE DECOMPOSITION

As stated in our previous technical report $Fe_2(SO_4)_3$ *is a cheap and relatively available compound which has no harmful effect on the environment*. It is seen in the experiments presented herein to once again **greatly accelerate** the **complete mineralisation** of this new series of phosphate ester simulants as well as the substituted aromatic compound nitro-o-xylene.

In this set of experiments **TOC (total organic carbon) analyses** complement for the first time the traditional CO_2 evolution curves. All aqueous dispersions of the model compounds were prepared by injecting the appropriate quantity of 10^{-1} M simulant solution (THF solvent) onto the reaction vessels' walls and letting the solvent evaporate in the air until no traces of solvent are left, and subsequently redissolving the simulants in water. The TiO_2 powder (P25, Degussa, 10 g/l) and appropriate catalytic agent (in this case, $Fe_2(SO_4)_3$) are then added, the solutions being stirred continuously.
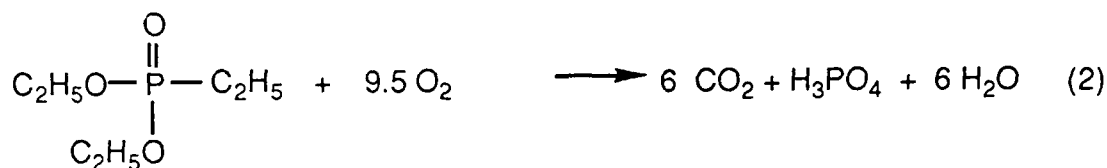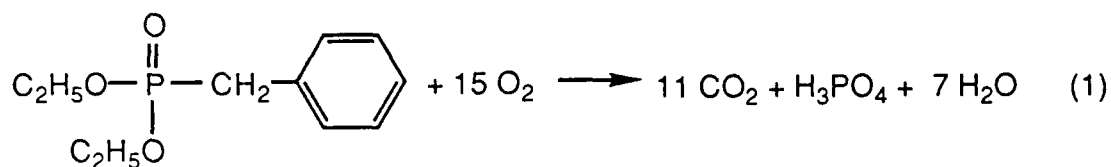
Fig. I illustrates the **effect** of **ferric sulfate** on the **total oxidative decomposition** (via organic carbon loss) of aqueous solutions of diethylbenzylphosphonate ($5x10^{-3}$M) in presence of H_2O_2 (O.3M) and TiO_2 (10 g/l) at 60ºC **in simulated sunlight**. In the

absence of ferric sulfate, the T.O.C. content of the solution declines relatively slowly. After a reaction time of 6 hours the solution still contains half of the organic carbon initially present . Addition of $Fe_2(SO_4)_3$ (5.10^{-3}M) accelerates the T.O.C. decay in a striking fashion. The measurement taken after 1 hour shows that ca 90% of the organophosphate has already been mineralized.

Further investigations were carried out in order to explore whether or not **ferric sulfate** was also effective in **catalysing** the **complete decomposition** of the **organophosphate** in the **absence of light**. This effect is indeed confirmed by the results shown in Figure 2. The decomposition was studied here in the dark at 50ºC. The hydrogen peroxide (total concentration 0.3M) was added here in three equal portions: in the beginning of the reaction and after 1 and 2 hours, respectively. In the presence of ferric sulfate the T.O.C. value declines very rapidly even though no light is employed to photo-activate the catalyst. The measurement effected after one hour shows that close to 80% of the phosphate has been mineralized completely after this lapse of time. It is also apparent from Figure 2 that the influence of the titanium dioxide on the catalytic dark reactions is relatively small.

The **oxidative destruction** of the **organophosphate** was also examined in solutions containing (apart from the hydrogen peroxide) only ferric sulfate. This led to the surprising and important discovery that **simulated sunlight enhances** this process even in the **absence of titanium dioxide**. Figure 3 displays the effect of sun light excitation on the T.O.C. decay. The light effect is clearly discernible in particular in the last part of the reaction where the illumination of the solution allows the mineralisation of the DBP to go rapidly to completion Further experiments showed that the **photoactive agent** in this process is **ferric sulfate** or a hydrolyzed form of it, i.e. **colloidal iron oxide**. Ferric sulfate, thus, plays a dual role in the mineralisation of DBP: it is a potent oxidation catalyst in the dark and this property is further enhanced by sun light excitation.

Investigations involving analysis of the **T.O.C. decay** were also performed for the second agent studied, i.e. **diethylethylphosphonate**, under identical reaction conditions and employing the same initiating techniques. These two simulants were found to obey the decomposition stoichiometries described in equations 1) and 2).

$$C_2H_5O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle C_2H_5O}{|}}{P}}-CH_2-\langle\text{benzene ring}\rangle + 15\,O_2 \longrightarrow 11\,CO_2 + H_3PO_4 + 7\,H_2O \quad (1)$$

$$C_2H_5O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle C_2H_5O}{|}}{P}}-C_2H_5 + 9.5\,O_2 \longrightarrow 6\,CO_2 + H_3PO_4 + 6\,H_2O \quad (2)$$

Results obtained with this simulant confirmed the trends observed for DBP: Under all three reaction initiating conditions the initial rates are similar, differences being noted primarily in the last stage of the reaction. The combined thermal/photolytic reaction triggering is the most efficient pathway where according to the TOC analyses the degradations are virtually complete. The positive synergistic influence of simultaneous heating and irradiation (or heating and subsequent irradiation) is quite apparent in both the diethylbenzylphosphonate and diethylethylphosphonate decays.

CATALYST, OXIDANT AND TIO2 INFLUENCE ON REACTION COURSE

When discussing the role of ferric sulfate in the rapid oxidation of the organophosphate compounds it should first be noted that ferric ions form a 1:1 complex with sulfate (association constant 1.41×10^4) in aqueous solution. At neutral pH this is likely to undergo condensation reactions to yield oligomers or polymers where the individual ferric sulfate units are linked through oxygen bridges. The extent of polymerisation has not yet been assessed under the present reaction conditions and further aggregation of these polymers to yield colloidal Fe_2O_3 or β-FeOOH cannot be excluded at this stage. Thus, the Fe(III) could be present in our solutions in different forms , the catalytically active one remaining yet to be determined. The catalytic intervention of such iron(III) species could occur via two different pathways. The first involves formation of an Fe (IV) complex formed by O-

transfer from hydrogen peroxide. This is a very powerful oxidant capable of attacking the organophosphate. As the organophosphate is oxidized Fe (IV) is regenerated into Fe (III) thus maintaining its catalytic status. Hydrogen peroxide is exhausted as a sacrificial oxidant. The second mode of decomposition is autocatlytic in nature. It would involve the reduction of Fe(III) to Fe(II) by the organophosphate. The Fe(II) would subsequently undergo a Fenton-type reaction with hydrogen peroxide generating hydroxyl radicals which in turn oxidize the CW simulant.
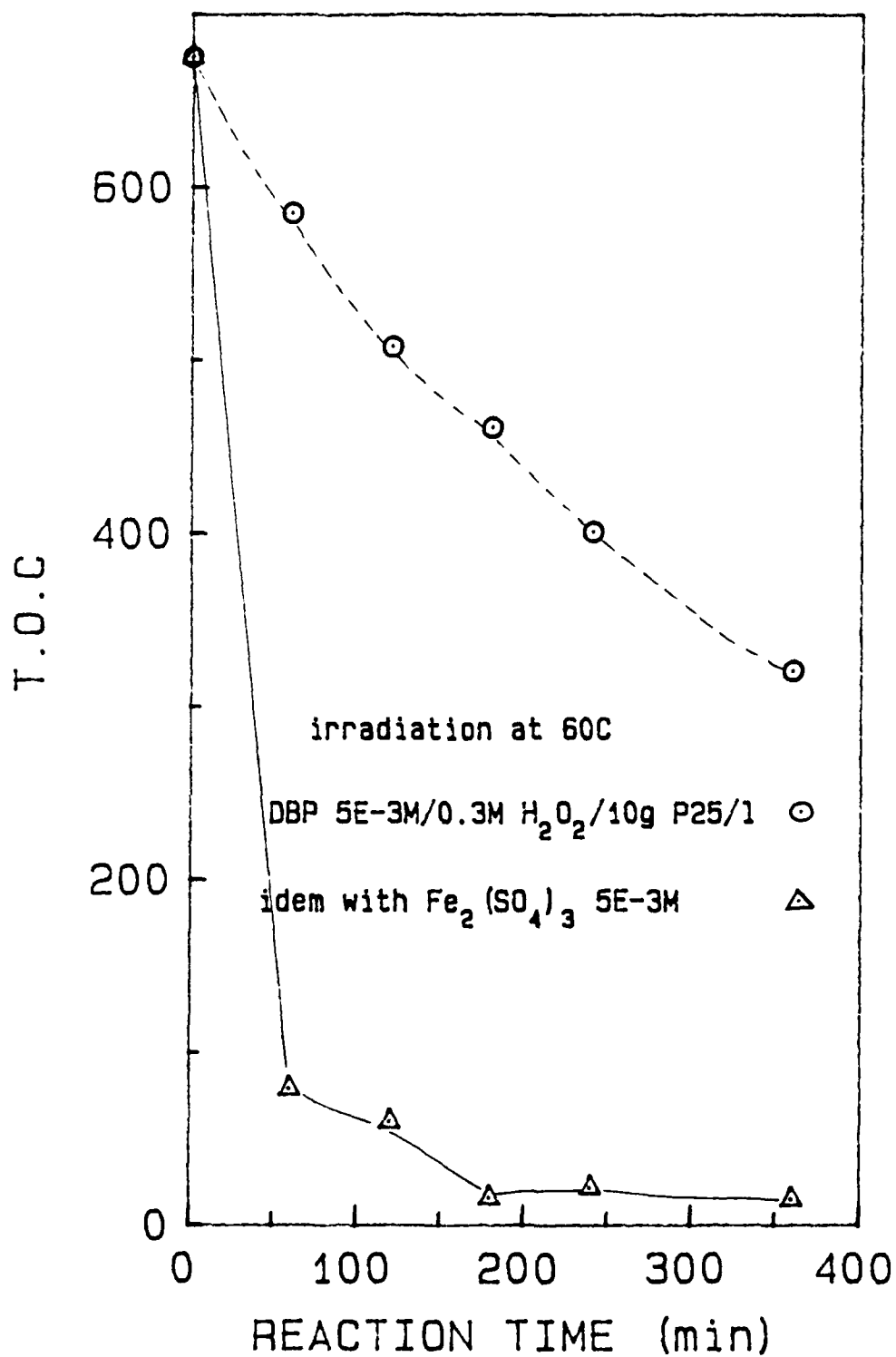
The sustaining action of TiO_2 in oxidations of simulants by H_2O_2 was again observed in particular in the decomposition of the second simulant. Apparently the disproportionation of H_2O_2 into oxygen and water competes with the oxidation of agent by this oxidant.

For these reasons present experiments are now being carried out between room temperature and 60°C (where H_2O_2 disproportionation is less efficient) and by addition of small aliquots of H_2O_2 at certain time intervals to attain the final H_2O_2 concentration of 0.3 M.
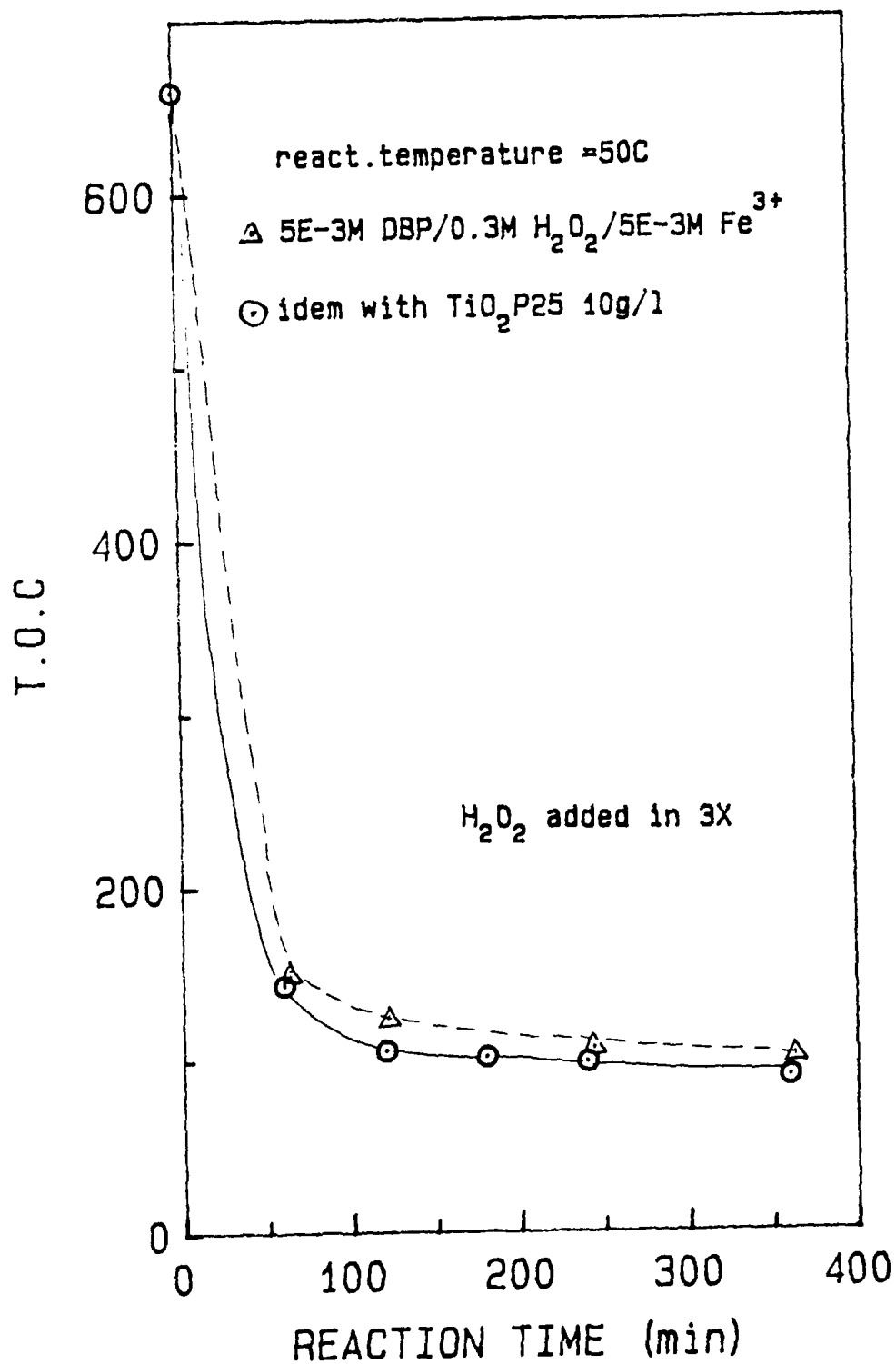
NOX DESTRUCTION

In order to emphasize this thermal/photolytic synergism the degradation of NOX by H_2O_2 was performed in two-steps. Fig. IV depicts both the absorption spectra (λ max = 310 nm) and TOC decay as a function of reaction time. Following the absorption decay the limiting plateau is attained rapidly under heating and stays constant upon solution illumination. In contrast there is a definite step between the thermal and irradiated plateaus in the TOC decay, a first threshold just being attained for the thermal decomposition when sample irradiation brings about an abrupt vertical drop in the decay curve. The oxidative destruction following irradiation was virtually complete according to the TOC results. The residual absorption spectrum is without a doubt due to absorption by various inorganic species generated in the decomposition. The totality of organic destruction in irradiated solutions proves the importance of the reaction with the semi-conductors photo-generated electrons not only in the capacity of producing strongly oxidizing radical species from the parent oxidant, but as a consequence of this formation the inhibition of the back reaction of the generated charge carriers (electrons and holes) allowing facile direct oxidation of the simulant by the valence band holes.

EFFECT OF Fe^{3+} ON DBP ONE-STEP DEGRADATION BY HYDROGEN PEROXIDE

irradiation at 60C

DBP 5E-3M/0.3M H_2O_2/10g P25/1 ⊙

idem with $Fe_2(SO_4)_3$ 5E-3M △

T.O.C

REACTION TIME (min)

DBP THERMAL DEGRADATION

react.temperature =50C

△ 5E-3M DBP/0.3M H_2O_2/5E-3M Fe^{3+}

⊙ idem with TiO_2 P25 10g/l

H_2O_2 added in 3X

T.O.C

REACTION TIME (min)

LIGHT EFFECT ON DBP DEGRADATION

react.temperature =50C

⊙ 5E-3M DBP/0.3M H_2O_2/5E-3M Fe^{3+}

△ idem with irradiation in Suntest

H_2O_2 added in 3X
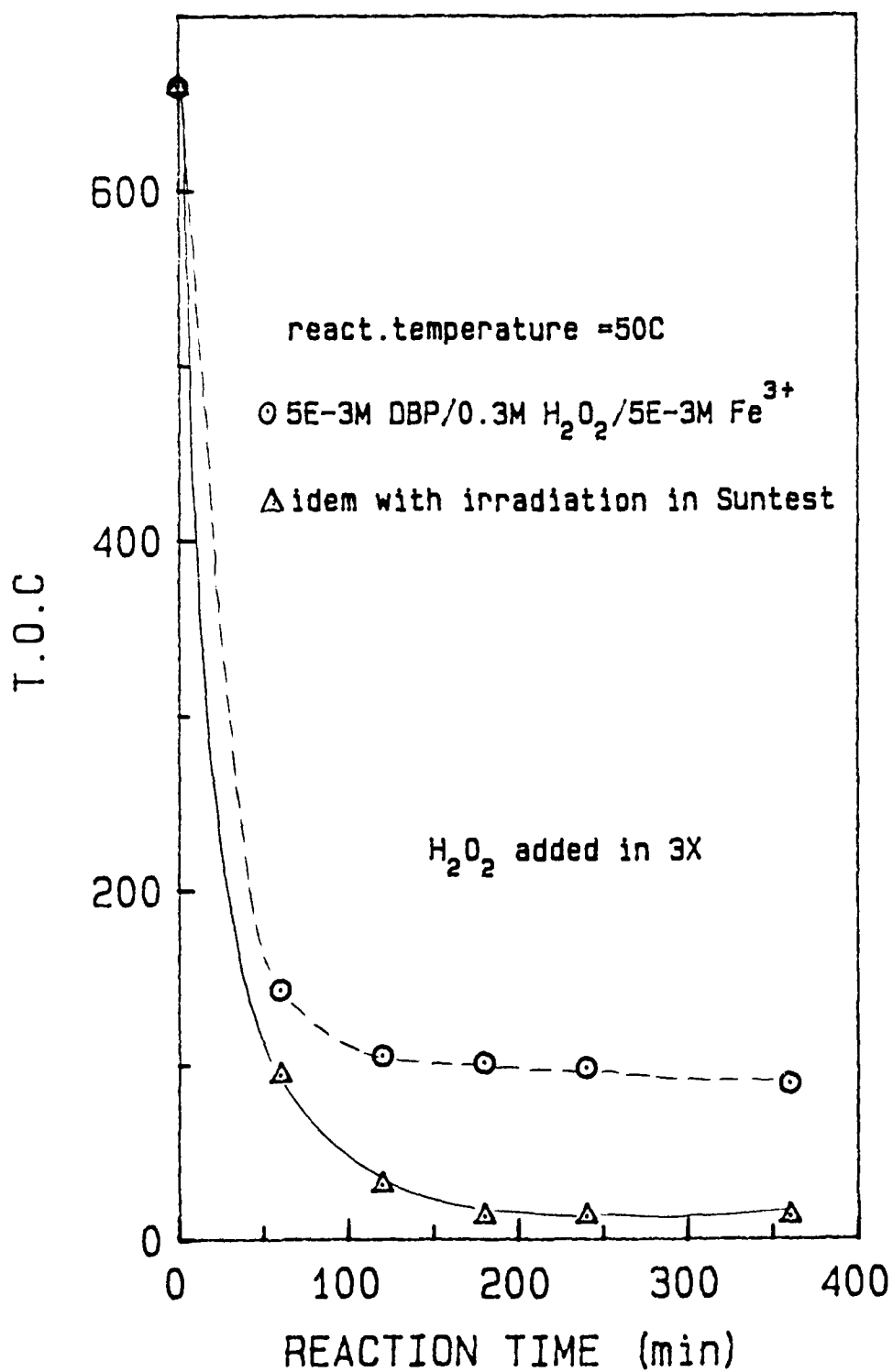
NOX TWO-STEP DEGRADATION BY H_2O_2

NOX non diluted

0.3M H_2O_2/5E-3M Fe_2 $(SO_4)_3$/70C

after 2h, add.P25 10g/l/0.1M H_2O_2

irrad.at 70C in reactor/O_2

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dark reac.   irradiation